(51) Int. Cl.: C 07 f
A 01 n. 9 36

FEDERAL REPUBLIC OF GERMANY

GERMAN PATENT OFFICE

(52) German Cl.: 12 o. 26/01
45 I.9 36

(10) (11) Patent Application Pub. 1 935 758

(21) Reference No.: P 19 35 758.5
(22) Application Date: 14 July 1969
(43) Publication Date: **19 February 1970**

Issue Priority: —

(30)	Country Priority:		
(32)	Date:	15 July 1968	27 June 1969
(33)	Country:	United Kingdom	
(31)	Reference No.:	33690-68	33690-69

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(54) **Title:** **Pesticide**

(61) **Addendum to:** —

(62) **Separation from:** —

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Notice per Article 7 § 1 Para. 2 No. 1 of the law of 09.04.1967 (BGB1.1S. 960):

DT 1 935 758

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"Insecticides 4"

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Pesticides

The invention pertains to new compounds with insecticidal and acaricidal properties, and preparation containing these compounds.

Subject of the invention are compounds with the general chemical structure

$$\begin{array}{l} \quad\;\; OR^1 \\ \quad\;\;\; | \\ X{=}P{-}Y{-}CH_2.CO.NR^2.CO_2R^3 \\ \quad\;\;\; | \\ \quad\;\;\; R \end{array} \qquad (I)$$

where R and R^1 , which may be equal or different, are aliphatic groups with 1 to 4 carbon atoms or aromatic groups,

where R^2 is a hydrogen atom or an aliphatic group with 1 to 4 carbon atoms,

where R^3 is an aliphatic, preferably an alkyl or alkenyl group with 1 to 10 carbon atoms,

and where X and Y, which may be the same or different, are oxygen or sulphur atoms.

The groups R, R^1 and R^2 may be saturated or unsaturated groups, for example alkoxyalkyl, alkyl, alkenyl, halogen alkyl or alkylthioalkyl groups, and which preferably are methyl or ethyl groups. Other preferred groups are the propyl, isopropyl, butyl, ethoxyethyl, methoxyethyl, allyl, and 2-chloroethyl group.

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When R and/or R^1 is an aromatic group, it may be a phenyl group or, for instance, a phenyl group substituted with low-molecular alkyl or halogen.

Group R^3 may be a methyl, ethyl, n-propyl, isopropyl, butyl, pentyl, etc. group. Alternatively, R^3 may be an alkenyl, alkinyl, alkoxyalkyl, or alkyl-thioalkyl group.

Compounds with the chemical structure I, in which X and Y are different, but the other groups are equal, may exist in isomere forms, in particular the forms O:P.S. and S:P.O. In the following, any statements made for one of these isomere forms also apply to the other.

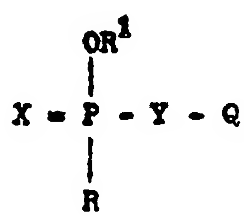
The compounds according to the invention have extraordinary interesting biological properties, especially in comparison to the organic phosphates known as pesticides. For example, they are especially active when applied to the soil. They are very active against Plutella maculipennis, Sitophilus granarius (horned beetle) and Myzus persicae.(Myzus persicae

is a green aphid that attacks sugar beets and potato plants, and spreads the yellow virus to sugar beets and different viral infections to potatoes, therfore weakening the infected plants. Some of the compounds according to the invention are especially active against spider mites (T. telarius), which are resistant against organophosphates being used as miticides.

Generally, the compounds according to the invention have higher activity than similar phosphates, and the activity of some of the compounds is even much higher. On one hand, the compounds are biodegradable and on the other hand, their effect lasts longer than that of other phosphates.

S-(N-Methoxycarbonyl-N-methyloarbamoyInethyl)-dimethyl-phosphonothiolothionate has an acute oral toxicity (LD_{50}) of 57 mg/kg in rats, and a favorable ratio of insecticidal properties vs. toxicity for mammals.

The compounds according to the invention can be manufactured with known methods. They are produced according to the invention by the reaction of a compound with the chemical structure



(II)

where R, R^1, X and Y have the above-indicated meanings, and Q is a hydrogen atom, an alkaline or ammonia ion or an organic cation with

an N-halogen acetyl carbamate with the general structure:

$$Hal.CH_2.CO\ NR^2CO_2R^3 \qquad (III)$$

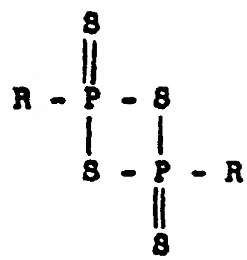
wherein R^2 and R^3 have the above-indicated meaning, and Hal is a halogen atom, i.e. chlorine, bromine or iodine, whereby the reaction - if Q is a hydrogen atom - takes place in the presence of an acid binder.

Acid-binding agents are, for example, alkaline carbonates like sodium or potassium carbonate and tertiary, organic bases like pyridine and triethylamine. The reaction can potentially be performed within a solvent. Suitable solvents are water, ketones, like acetone, methylethylketone and methylisobutylketone, dioxane, alcoholic substances like methanol, ethanol, and Isopropanol, ethers like diethyl ether and di-isopropyl ether, hydrocarbons like petroleum ether, benzene and toluene, halogenated hydrocarbons like chloroform, tetrachlorocarbon, methylene dichloride and chlorobenzene, and amides and nitriles like dimethylformamide, dimethylacetamide and acetone nitrile.

Preferred for the reaction is an alkaline salt like formula II sodium or potassium or ammonia salt with a formula III N-chloroacetyl-carbamate.

The formula II compounds can be produced with known methods as described, for example, by Chupp & Newallis, J.Org.Chem., (1962) 27, S. 3852, British patent specification 912,747, and Hoffman, Kagan und Carfield, J.A.C.S. (1959) 81, p. 148.

The formula I compounds of the invention, in which X and Y are both sulphur atoms, can also be produced by a reaction of the chemical structure:



(IV)

in which R has the above-indicated meaning, with a formula III N-halogen acetyl carbamate in the presence of an alcohol R^1OH, wherein R1 has the above-indicated meaning, and an acid-binding agent.

The transformation takes preferably place in the presence of a solvent, advantageously an excess of the alcohol R^1OH.

The acid-binding agent is preferably an alkyl carbonate like sodium or potassium carbonate, or a tertiary organic base, like pyridine or triathylamine.

The transformation can take place at about room temperature; however, if necessary, temperatures in the range from 0 °C to 100 °C can be used, whereby measures may have to be taken to prevent the pyrolysis or restructuring of the reacting components as well as the end products.

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The new compounds can be processed with different methods into pesticides, which generally contain the agent together with a carrier substance or a dilutant. The carrier can be fluid or solid, and may either be used for the dispersion of the agent or to form together with it a preparation, from which an easily dispersible agent can be produced at the application site.

Liquid compounds therefore contain the agent in the form of a solution or an emulsion, which is used alone or can be diluted with water or other dilution agents into a spray. In these cases, the carrier is a non-phytotoxic solvent or a non-phytotoxic emulsion base. Such compounds usually contain a netting or dispersion agent or an emulsifier. Other liquid embodiments are aerosols containing the agent together with a liquid carrier or propellant.

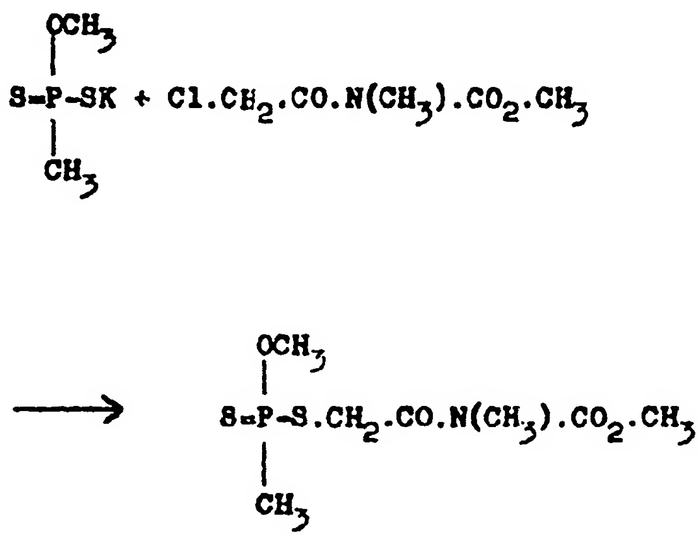
Solid embodiments are dust and nettable powders, granulates and pellets, and a semi-solid embodiment may be a paste, for example. Such products may contain inert solid or liquid dilution agents like clays, which themselves have netting properties, and/or contain netting, dispersion agents or emulsifiers, binders and/or adhesives. Solid products also include fumigation agents, which contain the active agent together with a solid, pyrotechnical component.

The compounds according to the invention can be used with compatible insecticides and/or fungicides.

The following embodiments illustrate the invention. Parts information refers to weight if not indicated otherwise. Information in weight and volume parts shall be interpreted as the g:ccm-ratio.

Embodiment 1

S-(N-Methoxycarbonyl-N-methylcarbamoylmethyl)-dimethyl-phosphonothiolothionate



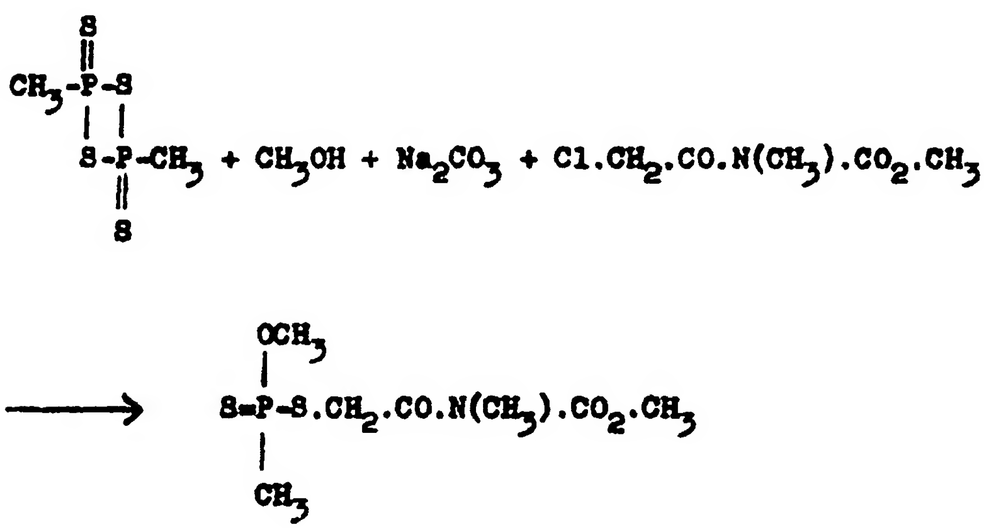
30 g (0.165 mol) potassium dimethylphosphonothiolo-thionate, F 180 °C solved in 140 ml acetone, were added to a solution of 24.9 g (0.15 mol) of methyl-N-chloroacetyl-N-methyl-carbamate in 40 ml acetone. The reaction was mildly exothermic. The reaction mixture was left standing for one day at room temperature. Then, potassium chloride (11.2 g, theory: 11.21 g) was filtered off, and the filtrate was distilled on the steam bath at 10 to 20 mm. The residue was dissolved in ether and washed with water. The ether solution was dried with Na_2SO_4, and evaporated at room temperature and 0.8 mm. The result were 38.95 g (95.9%)

of a white oil n_D^{20} 1,5485.

Calculated: $C_7H_{14}NPO_4S_2$: N 5,16; P 11,44; S 23,6%
Actual: N 5,3; P 11,25; S 23,6

Kp 172 to 174 °C/2.5 mm, n_D^{20} 1,5475.

Embodiment 2
S-(N-methoxycarbonyl-N-methylcarbamoylmethyl)-
dimethyl-phosphonothiolothionate

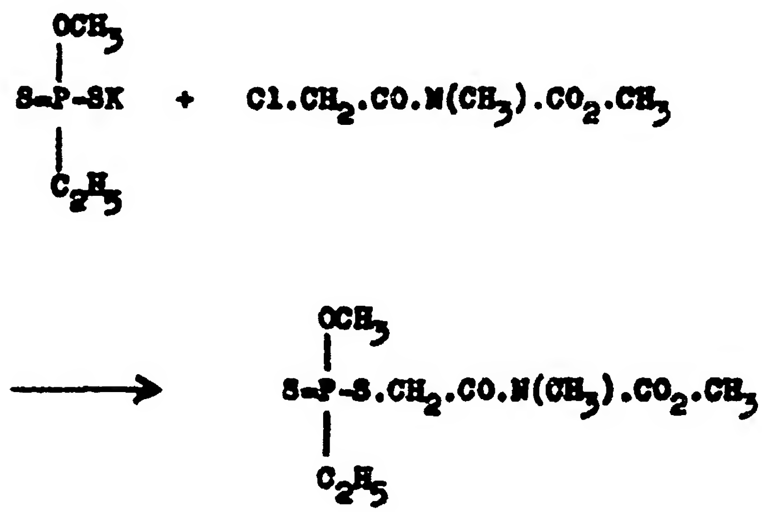


11.0 g (0.01 mol) of methyl-thionophosphinsulfide, produced as described by P.E. Nawallis, J.P. Chupp and L.C.C. Groenweghe, J. Org. Chem., (1962) 27, 3829, were dissolved in 30 ml of methanol (this step is exothermic). Added to the solution were 5.3 g (0.1 gEq) anhydrous sodium carbonate, initiating a strong development of carbon dioxide. In the next step, a solution of 15.7 g (0.095 mol) of methyl-N-chloroacetyl-N-methyl carbamate in 20 ml acetone was added, and the mixture was heated for 30 minutes to reflux. The precipitated solid was filtered off, and the filtrate

was heated for another 30 minutes to reflux, where no additional solid precipitate was found. Methanol and acetone were distilled out, and the residue was dissolved in ether and washed with 0.5 m sodium carbonate solution followed by water. The ether solution was separated and dried with Na_2SO_4. The dried solution was evaporated at room temperature and 2mm. The result were 24.05 g (93.4%) of a yellow oil, n^{20}_D 1,5460.

Embodiment 3

S-(N-Methoxycarbonyl-N-methylcarbamoylmethyl)-O-methyl-ethylphosphonothiolothionate

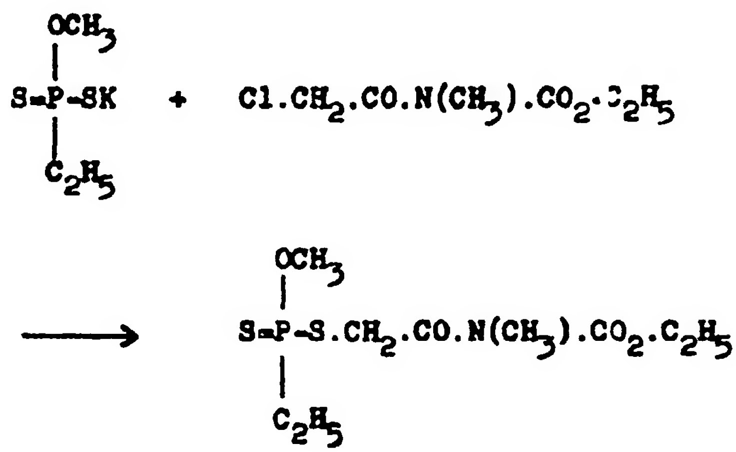


The method from embodiment 1 was repeated using potassium-O-methyl-ethylphosphonothiolothionate.
The result was a product of Kp 151°C/0,65 mm, n_D^{20} 1,5438.

Calculated: $C_8H_{16}NO_4PS_2$: S 22,45%
Actual: S 22,3

<u>Embodiment 4</u>

<u>S-(N-ethoxycarbonyl-N-methylcarbamoylmethyl)-O-methyl-ethylphosphonothiolothionate</u>



The method from embodiment 3 was repeated using ethyl-N-chloroacetyl-N-methylcarbamate. The result was a product of Kp 144°C/0,3 mm, n_D^{20} 1,5340.

Calculated: $C_9H_{18}NO_4PS_2$: S 21,4%
Actual: S 21,5

<u>Embodiment 5</u>

<u>S-(N-ethoxycarbonyl-N-methylcarbamoylmethyl)-O-ethyl-methylphosphonothiolothionate</u>

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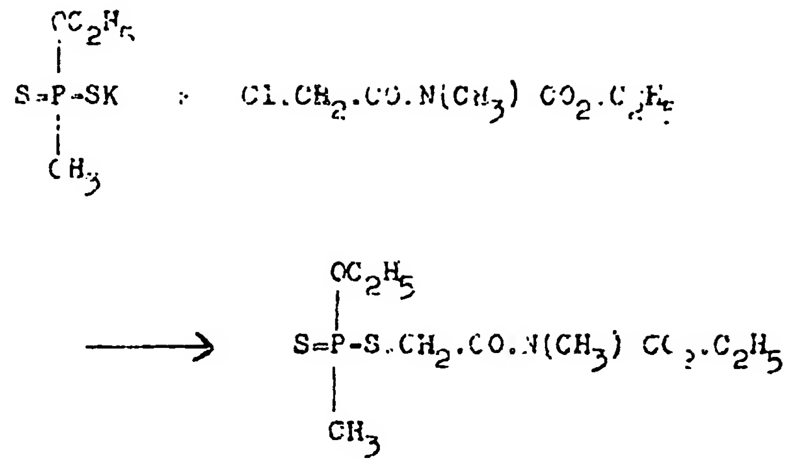


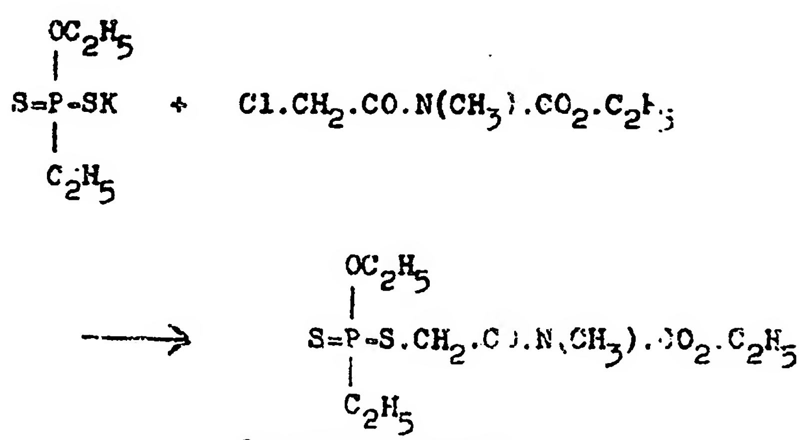
The method from embodiment 4 was repeated using potassium-O-ethyl-methyl-methylphosphonothiolothionate.

The result was a product with 38 bis 139°C/0,25 mm, n_D^{20} 1,5300.

Calculated: $C_9H_{18}NO_4PS_2$: S 21,4
Actual: S 21,3

Embodiment 6

S-(N-ethoxycarbonyl-N-methylcarbamoylmethyl)-diethyl-phosphonothiolothionate



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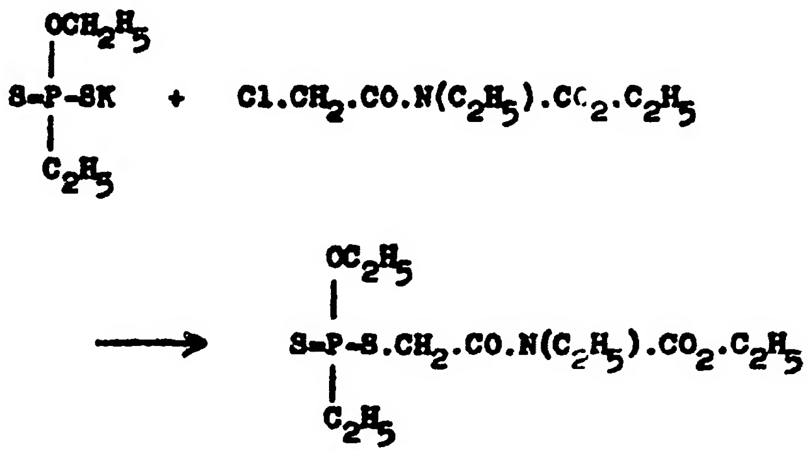
The method of embodiment 4 was repeated using potassium-diethyl-phosphonothiolothionate and 4 hours of boiling of the mixture at the reflux a product of 145 bis 146°C/0,35 mm, n_D^{20} 1,5270.

Calculated	$C_{10}H_{20}NO_4PS_2$:	S 20,45%
Actual		S 20,47

Embodiment 7

S-(N-ethoxycarbonyl-N-ethylcarbomoylmethyl)-diethyl-phosphonothiolothionate

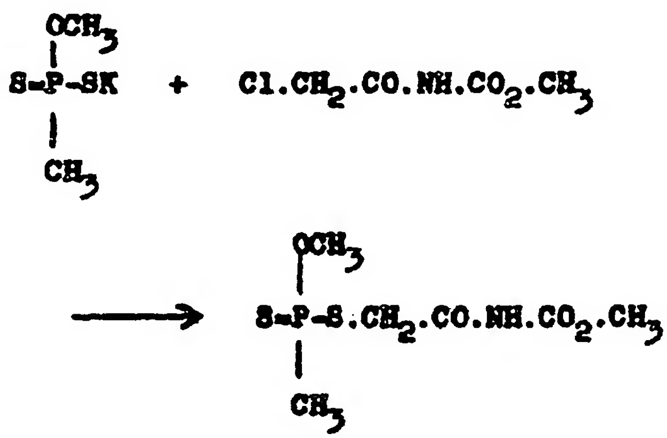


The method of embodiment 6 was repeated using ethyl-N-chloroacetyl-N-ethylcarbamate.
The result was a product of Kp 144°C/0,25 mm, n_D^{20} 1,5215.

Calculated	$C_{11}H_{22}NO_4PS_2$:	S 19,6%
Actual		S 19,8

Embodiment 8

S-(N-methoxycarbonyl-carbamoylmethyl)-diethyl-phosphonothiolothionate



The method for embodiment 1 was repeated using potassium-dimethyl-phosphonothiolothionate and methyl-N-chloroacetylcarbamate. Added to the oil that resulted after the acetone had been separated was ether followed by water and then chloroform. The watery layer was separated, and the solution in chloroform was dried with sodium sulfate. After separating the chloroform and recrystallization into toluene, the result were white platelets of F 108.5 to 109.3 °C.

Calculated: $C_6H_{12}NO_4PS_2$: P 12,0%
Actual: P 12,0

Embodiment 9

(N-methoxycarbonyl-N-methylcarbamoylmethyl-dimethyl-phosphonothioate

6.9 g (0.042 mol) potassium-dimethylphosphonothioate, dissolved in 30 ml acetone, were mixed with 6.62 g (0.04 mol) of methyl-N-chloroacetyl-N-methylcarbamate, dissolved in 10 ml acetone. The mixture was left standing at room temperature for 5 days. The solid substance (2.97 g, calculated quantity of potassium chloride = 2.98 g) was filtered off, and the filtrate was heated in the vapor bath at 10 to 20 mm. The residue was dissolved in chloroform, and washed with a small amount of water. The chloroform solution was separated, dried with sodium sulfate, and heated to 20 °C/2mm, resulting in a residue of 9.6 g of a brown oil. Through distillation, the result was a product of Kp 144 to 146 °C/ 0.5 mm, n_D^{20} , 1.5080.
Kp 144 bis 146°C/0,5 mm , n_D^{20} 1,5080.

Calculated: $C_7H_{14}NO_5PS$: S 12,55%
Actual: S 12,1

Embodiment 10

(N-ethoxycarbonyl-N-methylcarbamoylmethyl)-O-ethyl-methyl-phosphonothioate

The method of embodiment 1 was repeated using potassium-O-ethylmethylphosphonothioate and ethyl-N-chloroacetyl-N-methylcarbamate. The result was a product of Kp 139°C/0,3 mm, n_D^{20} 1,4958.

Calculated: $C_9H_{18}NO_5PS$: S 11,3%
Actual: S 11,1

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Embodiment 11

(N-ethoxycarbonyl-N-methylcarbomoylmethyl)-O-methyl-ethyl-phosphonothioate

The method of embodiment 1 was repeated using potassium-O-methylethylphosphonothioate and ethyl-N-chloroacetyl-N-methylcarbamate. The result was a product of 140°C/0,25 mm, n_D^{20} 1,4990.

Calculated: $C_9H_{18}NO_5PS$: S 11,3%
Actual: S 11,3

Embodiment 12

(N-methoxycarbonyl-N-methylcarbamoylmethyl)-diethyl-phosphonothioate

A solution of 20.7 g (0.125 mol) of methyl-N-chloroacetyl-N-methylocarbamate in 50 ml acetone was added to a solution of 24.0 g (0.123 mol) of potassium-O-ethyl-ethylphosphonothioate in 200 ml acetone, whereby potassium chloride immediately precipitated. The mixture was heated for 4 ½ hours on the vapor bath for reflux and filtered. The acetone was evaporated under reduced pressure at 50 to 60 °C, and the remaining oil was dissolved in 100 ml benzene. The benzene solution was washed with 20 ml 2n sodium carbonate and then with 20 ml of a 1% sodium chloride solution, and dried via anhydrous sodium sulfate. The benzene was distilled under reduced pressure at 50 to 60 °C. The result was 33.2 g (94%) of an oil with Kp 140°C/0,3 mm, n_D^{20} 1,4985.

Calculated: $C_9H_{18}NO_5PS$: S 11,3%
Actual: S 11,3

Embodiment 13

(N-ethoxycarbonyl-N-methylcarbamoylmethyl)-diethyl-phosphonothioate

The method of embodiment 1 was repeated using potassium-diethylphosphonothioate and ethyl-N-chloroacetyl-N-methylcarbamate. The result is a product with

Kp 142°C/0,3 mm, n_D^{20} 1,4930.

Calculated: $C_{10}H_{20}NO_5PS$: S 10,77%
Actual: S 10,76

Using the method for embodiment 1, the following compounds were produced from the necessary base materials:

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Embodiment	Compound	Kp°C/mm	n_D^{20}	Gross Formula	Analysis Calculated % P	Calculated % S	Actual % P	Actual % S
14	S-(N-Methoxycarbonyl-N-methylcarbamoylmethyl)-dimethyl phosphonothiolothionate	139-140/0.3	1.5385	$C_8H_{16}NO_4PS_2$		22.65		22.46
15	(N-Methoxycarbonyl-N-ethylcarbamoylmethyl)-dimethyl-phosphonothioate	135-136/0.3	1.4999	$C_8H_{16}NO_5PS$		12.00		11.90
16	S-(N-Ethoxycarbonyl-N-methylcarbamoylmethyl)-O-propylethyl-phosphonothiolothionate	139-140/0.2	1.5368	$C_8H_{16}NO_4PS_2$		22.25		22.46
17	S-(N-Methoxycarbonyl-N-methylcarbamoylmethyl)-O-propylethyl-phosphonothiolothionate	152-3/0.3	1.5305	$C_{10}H_{20}NO_4PS_2$		20.45		20.45
18	S-(N-Ethoxycarbonyl-N-methylcarbamoylmethyl)-O-propyl-ethyl-phosphonothiolothionate	151-2/0.15	1.5221	$C_{11}H_{22}NO_4PS_2$		19.43		19.57
19	S-(N-Methoxycarbonyl-N-methylcarbamoylmethyl)-O-butyl-ethyl-phosphonothiolothionate	160-1/0.3	1.5256	$C_{11}H_{22}NO_4PS_2$		19.79		19.57

Embodiment	Compound	Kp °C/mm	n_D^{20}	Gross Formula	Analysis Calculated % P	Calculated % S	Actual % P	Actual % S
20	S-(N-Ethoxycarbonyl-N-methyl-carbamoylmethyl)-O-butyl-ethyl-phosphonothiolothionate	161-2/0.2	1.5188	$C_{12}H_{24}NO_4PS_2$		18.78		18.77
21	S-(N-Methoxycarbonyl-N-methylcarbamoylmethyl)-O-allyl-ethyl-phosphono-thiolothionate	158-9/0.25	1.5418		10.0		10.0	
22	S-(N-Ethoxycarbonyl-N-methyl-carbamoylmethyl)-O-allyl-ethyl-phosphonothiolothionate	161-2/0.2	1.5319			19.8		19.7
23	S-(N-Methoxycarbonyl-N-methyl-carbamoylmethyl)-dimethyl-phosphonothioate		whitish acetone prisms	$C_6H_{12}NO_5PS$	12.90		12.86	
24	S-(N-Methoxycarbonyl-N-methyl-carbamoylmethyl)-O-2-chhlorethyl-ethyl-phosphonothiolothionate		1.5461			19.8		19.2
25	S-(N-Ethoxycarbonyl-N-methyl-carbamoylmethyl)-O-2-chhlorethyl-ethyl-phosphonothiolothionate		1.5329			18.3		18.4

Embodiment	Compound	Kp°C/mm	n_D^{20}	Gross Formula	Analysis Calculated % P	Calculated % S	Actual % P	Actual % S
26	(N-Methoxycarbonyl-carbamoylmethyl)-diethyl-phosphonothioate		1.5039 Red Oil	$C_8H_{16}NO_5PS$	11.7		11.5	
27	(N-Ethoxycarbonyl-N-methyl-carbamoylmethyl)-dimethyl-phosphonothiolothionate	134-135/0.3	1.4998	$C_8H_{16}NO_5PS$		11.9		11.9
28	(N-Methoxycarbonyl-N-methyl-carbamoylmethyl)-O-ethyl-methyl-phosphonohioate	Pale brown needles of propane-2-ol		$C_8H_{16}NO_4PS_2$		23.0		22.5
29	S-(N-Methoxycarbonyl-N-methyl-carbamoylmethyl)-O-propyl-methyl-phosphonothiolothionate	140-141/0.25	1.5350	$C_9H_{18}NO_4PS_2$		22.0		21.4
30	S-(N-Methoxycarbonyl-N-methyl-carbamoylmethyl)-diethyl-phosphono-thiolothionate	154/0.4	1.5360	$C_9H_{18}NO_4PS_2$		21.1		21.4
31	S-(N-Methoxycarbonyl-N-methyl-carbamoylmethyl)-dipropyl-phosphonothiolo-thionate		1.5239 Brown Oil	$C_{11}H_{22}NO_4PS_2$		19.3		19.6

Embo-dimen	Compound	Kp°C/mm	n_D^{20}	Gross Formula	Analysis Calculated % P	Calculated % S	Actual % P	Actual % S
32	S-(N-Methoxycarbonyl-N-methyl-carbamoylmethyl)-dibutyl-phosphonothiolothionate	152/0.05	1.5205	$C_{13}H_{26}NO_4PS_2$		17.7		18.0
33	S-(N-Allyloxycarbonyl-N-methyl-carbamoylmethyl)-diethyl-phosphonothiolothionate	158-159/0.3	1.5349	$C_{11}H_{20}NO_4PS_2$	9.4		9.5	
34	S-(N-Hexyloxycarbonyl-N-methyl-carbamoylmethyl)-diethyl-phosphonothiolothionate	178-179.5/0.3	1.5124	$C_{14}H_{28}NO_4PS_2$	8.2		8.4	
35	S-(N-Methoxycarbonyl-N-methyl-carbamoylmethyl)-O-mmethyl-phenyl-phosphonothiolothionate		1.6040 (Brown Oil)	$C_{11}H_{14}NO_4PS_2$	9.7		9.7	
36	S-(N-Ethoxycarbonyl-N-methyl-carbamoylmethyl)-O-methyl-phenyl-phosphonothiolothionate		1.5895 (Brown Oil)	$C_{12}H_{16}NO_4PS_2$	9.3		9.3	
37	S-(N-Methoxycarbonyl-N-methyl-carbamoylmethyl)-O-methyl-phenyl-phosphonothiolothionate		1.5915 (Brown Oil)	$C_{12}H_{16}NO_4PS_2$	9.4		9.3	

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Embodimen	Compound	Kp°C/mm	n_D^{20}	Gross Formula	Analysis Calculated % P	Calculated % S	Actual % P	Actual % S
38	S-(N-Ethoxycarbonyl-N-methyl-carbamoylmethyl)-O-methyl-phenyl-phosphonothiolothionate		1.5742 (Brown Oil)	$C_{13}H_{18}NO_4PS_2$	9.0		8.9	
39	S-(N-Ethoxycarbonyl-N-methyl-carbamoylmethyl)-O-2-ethoxyethyl-ethyl-phosphonothiolothionate		1.5218	$C_{12}H_{24}NO_5PS_2$		18.3		17.9
40	S-(N-Methoxycarbonyl-N-methyl-carbamoylmethyl)-O-2-ethoxyethyl-ethyl-phosphonothiolothionate		1.5289	$C_{11}H_{22}NO_5PS_2$		18.8		18.7
41	S-(N-Methoxycarbonyl-N-methyl-carbamoylmethyl)-di-isopropyl-phosphonothiolothionate	149-150/0.3	1.5251	$C_{11}H_{22}NO_4PS_2$	9.8		9.5	
42	S-(N-Methoxycarbonyl-N-methyl-carbamoylmethyl)-di-a-butyl-phosphonothiolothionate		1.5205	$C_{13}H_{26}NO_4PS_2$	8.3		8.7	
43	S-(N-Ethoxycarbonyl-N-methyl-carbamoylmethyl)-O-ethyl-methyl-phosphonothiolothionate	F 88 - 88.5 White prisms of propane-2-ol		$C_7H_{14}NO_4PS_2$		24.0		23.6

Embodiment	Compound	Kp°C/mm	n_D^{20}	Gross Formula	Analysis Calculated % P	Analysis Calculated % S	Analysis Actual % P	Analysis Actual % S
44	(N-Methoxycarbonyl-N-methyl-carbamoylmethyl)-O-propyl-methyl-phosphonothioate	140-142/0.3	1.4957	$C_9H_{18}NO_5PS$		11.3		11.3
45	S-(N-Methoxycarbonyl-N-methyl-carbamoylmethyl)-dibutyl-phosphonothiolo-thionate	F 41-45 (white almonds of petroleum ether Kp 40-60)		$C_{12}H_{24}NO_4PS_2$		18.5		18.8
46	S-(N-Methoxycarbonyl-N-methyl-carbamoylmethyl)-dipropyl-phosphonothiolo-thionate	F 73-75 (white platelets of petroleum ether Kp 40-60)		$C_{10}H_{20}NO_4PS_2$		21.6		21.1
47	S-(N-Methoxycarbonyl-N-methyl-carbamoylmethyl)-O-butyl-s-butyl-phosphono-thiolothionate		1.5206	$C_{13}H_{26}NO_4PS_2$		17.6		18.0
48	S-(N-Methoxycarbonyl-N-methyl-carbamoyl-methyl)-O-isopropyl-propyl-phosphonothiolothionate	160 / 0.5	1.5295	$C_{11}H_{22}NO_4PS_2$		20.5		19.6

Embodiment	Compound	Kp°C/mm	n_D^{20}	Gross Formula	Analysis Calculated % P	Analysis Calculated % S	Analysis Actual % P	Analysis Actual % S
49	S-(N-Ethoxycarbonyl-N-methyl-carbamoylmethyl)-dimethyl-phosphonothiolothionate		1.5298 Yellow Oil	$C_{11}H_{22}NO_4PS_2$		20.2		19.6
50	S-(N-Ethoxycarbonyl-N-methyl-carbamoylmethyl)-dimethyl-phosphonothiolothionate		1.4936 Yellow Oil	$C_{11}H_{22}NO_5PS$	10.3		10.0	
51	S-(N-Ethoxycarbonyl-N-methyl-carbamoylmethyl)-dimethyl-phosphonothiolothionate		1.4928 Orange Oil	$C_{11}H_{22}NO_5PS$	10.0		10.0	

Preparations

The products of the embodiments were used to produce different emulsifiable concentrates, namely:

1) 4 parts agent were mixed with 10 parts polyethylene-glycolic ether (Lissapol NX), and the mixture was topped off with acetone to a total of 100 volume parts.

2) 25 parts agent, 4 parts of calciumdodecylbenzo-sulfonate and 4 parts of a non-ionic emulsifier were topped off with heavy petrol to 100 volume parts.

5) 80 parts agent and 20 parts of a mixture of non-ionic and anionic emulsifiers (Agrilan A of Lankro Chemicals Limited) were topped off with butanol to a total of 100 volume parts.

All of these preparations were diluted with water to their necessary degree of concentration.

A granulate was made as follows:

5 g agent were suspended in 7 g diacetone alcohol, and the suspension was thoroughly mixed with 87 g of fuller earth granules with diameters of 353 to 840 µm. The resulting granulate could be directly applied to the soil.

Biological Effect

Test for systemic effect against aphids when applied to the soil

One agent in the form of an emulsifiable concentrate was diluted with water at an active concentration of 500 ppm. 20 ml of this solution were applied by pipette around the

stem of broad bean plants inside a pot with a diameter of 7.5 cm. Immediately after the treatment, the plants were infected with aphis fabae, and 2 days later the killing rate was determined by counting. Another series of plants was infected with aphis fabae 3 days after having been treated with the agent, and the counting took place 48 hours later. Yet another series of plants was infected with aphids 5 days after the treatment, and the counting again took place 48 hours later. The results are summarized in Table I:

Table I - Systemic Effect against Aphis fabae

Compound of Embodiment #	Agent Concentration	% killed			Agent Concentration	% killed with Dimefox		
		2 days	5 days	7 days		2 days	5 days	7 days
1 and 2	500 ppm	97	100	100	500 ppm	98	100	56
1 and 2	250 ppm	100	100	99	250 ppm	99	14	0
3	500 ppm	100	100	100				
4	250 ppm	95	100	95				
5	250 ppm	* 67	91	97				
6	500 ppm	93	100	99	500 ppm	98	100	56
6	250 ppm	98	90	97	250 ppm	99	48	0
7	250 ppm	95	99	97				
8	250 ppm	99	98	99				
9	250 ppm	100	100	97	250 ppm	99	48	0
10	250 ppm	100	100	100	250 ppm	99	48	0
11	250 ppm	99	92	94	250 ppm	100	72	28
12	250 ppm	100	100	100	250 ppm	99	14	0
12	100 ppm	100	99	100	100 ppm	2	6	100
13	250 ppm	99	100	100	250 ppm	53	2	0
14	250 ppm	85	100	100	250 ppm	58	29	3
15	250 ppm	99	100	99	250 ppm	58	29	3

Table I (continued) - Systemic Effect against Aphis fabae

Embo-diment #	Agent Concentration	% killed			Agent Concentration	% killed with Dimefox		
		2 days	5 days	7 days		2 days	5 days	7 days
16	250 ppm	93	100	76	250 ppm	58	29	3
17	250 ppm	85	100	99	250 ppm	58	29	3
18	250 ppm	x 26	100	37	250 ppm	97	33	4
21	250 ppm	x 69	99	92	250 ppm	97	72	1
23	250 ppm	100	100	97	250 ppm	97	33	4
26	250 ppm	100	100	100	250 ppm	96	60	27
27	100 ppm	100	100	100	250 ppm	97	67	65
28	100 ppm	100	100	100	250 ppm	97	67	65
28	250 ppm	98	100	99	250 ppm	24	34	12
28	3,36kg/ha	86	100	100	3,36kg/ha	0	74	58
33	250 ppm	96	99	84	250 ppm	97	72	1
34	250 ppm	x 1	100	100	250 ppm	97	67	57

x Slowly working compounds

Additional tests for systemic effect against aphids

1. Killing of black and green aphids on rice plants

The soil was soaked with an emulsifiable concentrate of the agents (compound of embodiments 1 and 2).
The results were as follows:

Agent concentration, kg/ha	% killed
2.24	95% in 24 hours 100% in 48 hours Reinfected 1 week after treatment 90% killed in 24 hours
0.56	90% in 24 hours 98% in 48 hours 100% in 6 days

2. Killing of green aphids on tobacco plants

The compound of embodiments 1 and 2 was applied to sandy, loamy soil in the form of granules. The results were as follows:

Agent concentration kg/ha	% killed after 5 Weeks
8.96	100
4.48	100

During the test, the plants were reinfected with aphids. No phytotoxicity against the tobacco plants was noticed.

3. Killing of green aphids on cotton plants

The soil was soaked with an emulsifiable concentrate of the compound of embodiments 1 and 2. Phorate was used for

comparison purposes. The results were as follows:

Agent concentration kg/he	Number of live aphids per plant after 7	10	16	20 Days
2.24	30	8	0	1
1.12	3	21	0	1
0.48	47	30	3	4
Phorate 2.24	12	25	24	9
Phorate 1.12	75	105	60	95
untreated	90	125	80	125

During the test, the plants were reinfected with aphids. No phytotoxicity against the cotton plants was noticed.

Test of effect as contact poison against Aphis fabae

The host plants for this test were again viola fabae (field beans. An active agent was diluted with water to a concentration of 100 as well as 30, 10, 3 and 1 ppm, and applied to the plants by immersion. 48 hours after the treatment, the percentage of dead aphids was determined. Parallel tests for comparison using γ-benzo-hexachloride were also conducted. The results are listed in Table II.

Table II - Effect as Contact Poison against Aphis fabae

Compound of Embodiment #	% killed					% killed with γ-Benzohexachloride		
	100 ppm	30 ppm	10 ppm	3 ppm	1 ppm	100 ppm	30 ppm	10 ppm
1 and 2	99+	99	96	41	3	99	65	45
3	100	99	94	61	16			
4			83	21	31			
5			72	48	7			
6	100	100	100	70	68			
7	98	89	65					
9			99	60	59			
10			100	99	62			
11			99	70	49			
12	100	100	100	100	67			
13	100	100	89	92	50	91	34	12
14	100	83	37	-	-	91	34	12
15	100	99	86	-	-	91	34	12
16	100	96	53	-	-	91	34	12
17	-	-	100	84	26	96	63	4

Table II (continued) - Effect as Contact Poison against Aphis fabae

'Compound of Embo-diment #	% killed					% killed with γ-Benzohexachloride		
	100 ppm	30 ppm	10 ppm	3 ppm	1 ppm	100 ppm	30 ppm	10 ppm
18	100	100	91	-	-	91	34	12
19	99	89	95	-	-	91	34	12
20	99	98	89	-	-	91	34	12
22	100	100	88	-	-	98	14	4
23	100	100	93	-	-	91	34	12
24	99	100	99	-	-	98	14	4
25	100	96	86	-	-	98	14	4
26	100	100	97	-	-	99	33	6
27	-	-	100	99	99	99	60	9
28	100	100	100	99	70	99	60	9
29	100	100	99	-	-	82	34	6
30	100	100	94	-	-	100	95	15
31	100	100	100	-	-	100	100	65
33	100	100	93	-	-	98	14	4
34	100	100	99	-	-	98	14	4
39	98	66	70	-	-	99	33	6

Test for effectiveness as contact poison against Myzus persicae

The Myzus persicae used for the test were resistant against dimethoate. An agent preparation was diluted with water, so that the active agent concentration was 100 as well as 30, 10, 3 and 1 ppm, and the agent was applied to the plants (Rapas brassicus napus) by immersion. The percentage of dead aphids was determined after 24 hours. The comparative agent was again γ-benzo-hexachloride.

The results are summarized in Table III. The test results for dimetonemethyl, dimethoate, and malathion are also listed in Table III.

Table III - Effect as Contact Poison against Myzus persicae

Compound of Embodiment #	% killed					% killed with γ-Benzohexachloride		
	100 ppm	30 ppm	10 ppm	3 ppm	1 ppm	100 ppm	30 ppm	10 ppm
1 and 2	100	100	58	-	-	100	73	9
6	100	100	100	50	25	100	87	22
12	100	100	57	-	-			
21	100	100	44	-	-	100	46	18
22	100	100	79	-	-	100	46	18
24	100	100	96	-	-	100	46	18
25	100	100	100	-	-	100	46	18
26	100	100	100	-	-	100	73	9
27	100	100	100	94	44	100	73	9
28	100	100	6	-	-	100	73	9
29	100	100	100	-	-	100	73	9
31	100	100	50	-	-	100	85	32
33	100	100	97	-	-	100	46	18
34	100	100	100	50	25	100	87	22
Demetonemethyl	100	24	5	-	-			
Dimethoate	69	-	-	-	-			
Malathion	2	-	-	-	-			

Test for the duration of the systemic effect against Myzus persicae

The agent was applied to the soil in the form of a watery dispersion with a concentration of 250 ppm. The host plant was Chinese cabbage. Myzus persicae was applied to the plants 1 and 20 days after the treatment. Comparative tests were conducted with Dimefox. The results are summarized in Table IV.

Table IV

Myzus persicae -> Durational test of the systemic effectiveness

	% killed, days after treatment	
	1	20
Dimefox	99	7
Embodiment 1 und 2	97	76
Embodiment 6	91	95
Embodiment 7	-	100
Embodiment 12	-	100
Embodiment 18	-	100
Embodiment 44	-	100

Horticultural Effectiveness Test against Aphids

1) Sugar beet plants were sprayed with a watery dispersion of the agent with an agent concentration of 200 ppm. 5 and 18 days after the treatment, the total number of aphids on 6 plants was counted. The results were as follows:

Compound	Total # of aphids on 6 plants after	
	5 days	18 days
Embodiments 1 and 2	2	2
Embodiment 12	0	0
Demeton-methyl	0	29
Untreated	39	57

2) Green apples were sprayed with a watery dispersion of the compounds of embodiments 1 and 2 with a concentration of 200 ppm. The aphids were killed completely while the number of aphids on the untreated apples increased in the time period from the treatment to the count by 14 (% *(illegible)*).

3) The compound of embodiments 1 and 2 was tested against Rhopalosiphum insertum (pre-blossom aphid on fruit trees). It was applied prior to the opening of the blossoms in the form of a watery dispersion with a concentration of 200 ppm. The comparative test was conducted with dimethoate. The counts were taken 5 and 26 days after the treatment. The results were as follows:

Compound	% Infected Blossoms		
	Before Treatment	After Treatment	
		5 days	26 days
Embodiments 1 & 2	79	7	35
Dimethoate	88	40	94
untreated	86	90	95

Test for effectiveness as contact poison against Tetranychus telarius.

Schradan-resistent as well as Schradan-non-resistent strains of tetranychus telarius (red spider) were used; the host plants were dwarf beans.

The agent was applied in the form of a watery dispersion with a concentration 100 as well as 20 and 10 ppm by immersion. The percentage of spiders killed was determined after 48 hours. Comparative tests were conducted with mecarbam and parathion.
The results are summarized in Table V.

Table V

Effect as Contact Poison against Tetranychus Telarius

Compound of Embodiment	% of non-resistant spiders killed			% of resistant spiders killed		
	100	30	10 ppm	100	30	10 ppm
1 and 2	100	99	98	100	100	94
3	100	98	76	63	29	50
4	100	89	81	96	65	50
5	-	100	100	100	82	78
6	100	100	93	100	84	44
7	100	100	100	98	99	65
8	99	92	66	71	56	45
9	100	99	100	100	98	93
10	100	100	98	-	100	92
11	100	91	91	95	77	52
12	100	100	96	100	98	87
13	100	95	85	98	75	64
14	100	98	95	98	95	61
15	100	100	99	-	99	89
17	98	95	62			
18	99	93	92			
19	100	95	84	91	83	74
20	96	93	92			
23	99	99	97			
24	99	90	84			
25	99	94	77			
27	100	100	97			
28	100	100	92	100	93	85
29				94	92	94
30	97	83	57			
Mecarbam	93	86	62			
Parathion	-	78	-			

ORIGINAL INSPECTED

In another test series, the effect of the compound of embodiments 1 and 2 as contact poison was compared to that of known insecticides. The results are summarized in Table VI.

Table VI

Effectiveness as Contact Poison against Tetranychus Telarius

	% Killed					
	Non-resistant Spider			Resistant Spider		
	100	30	10	100	30	10 ppm
Compound of Embodiments 1+2	100	96	93	100	100	94
Azinphos-methyl	100	95	95	80	58	44
Demeton-methyl	100	98	97	59	60	44
Dimethoate				61	43	42
Malathion	95	95	43	47	32	25
Mecarbam	100	96	96	94	63	22
Parathion	91	89	67	43	9	-
Phenkapton	100	99	99	83	86	74
Schradan	76	-	-	38	-	-

Test of systemic effectiveness against Tetranychus Telarius

For this test, a non-resistant strain of tetranychus telarius was used. The host plants were dwarf beans. The spiders were applied to the plants and 24 hours later the agent in concentrations of 300 as well as 100, 30 and 10 ppm was applied to the soil. The percentage of spiders killed was determined 48 hours after the treatment. The results are as follows:

Compound	% killed at 300	100	30	10 ppm
Embodiment 15	-	100	93	68
Dimefox	97	90	65	19

Test of effectiveness as contact poison against maculi-pennis

Rape (brassica napus) was treated by immersion with a watery agent dispersion at a concentration of 100, 30 and 10 ppm. After the plants had dried they were infected with larvae of P. maculipennis, so that the poison was applied through skin contact and ingestion.

The percentage of fatalities was determined 48 hours after the larvae had been applied to the plants. The results are summarized in Table VII.

Table VII

Effectiveness as contact poison against Plutella maculipennis

Compound of Embodiment	% killed			% killed with DDT		
	100	30	10 ppm	100	30	10 ppm
1 and 2	100	100	-			
3	100	100	28			
4	100	89	5			
5	100	100	70			
6	100	75	28			
7	90	100	65			
9	94	89	63			
10	100	82	43			
13	98	75	64			
17	95	100	80	95	89	-
18	100	100	100	100	100	80
19	100	100	85	95	89	-
20	100	100	100	100	100	80
25	100	94	10	95	26	-
33	100	100	28	95	26	-

Test of effectiveness as contact poison against Coleoptera

Three types of coleoptera - sitophilus granarius, phaedon cochleariae (mustard beetle adults) and tribolium - were treated with compounds described in the invention at concentrations of 300, 100 and 30 ppm. The agent was applied by micrometer syringe. The percentage of beetles killed was determined in the case of S. granarius one week after treatment, and in the case of P. cochleariae and tribolium 30 days after treatment. Parallel tests were conducted with mecarbam. The results are summarized in Table VIII.

Table VIII
Test against Coleoptera

1. Sitophilus granarius

Compound of Emb.	% killed 300	100	30 ppm	% killed with Mecarbam 300	100	30 ppm
1 and 2	100	92	12	100	76	-
3	100					
4	100					
5	100					
6	100	100	88	100	76	-
11	100	100	96	100	48	-
13	100	100	71	100	33	-

2. Phaedon Cochleariae

Compound of Emb.	% killed 300	100	30	10 ppm	% killed with Mecarbam 100	30 ppm
1 and 2	100	100	20	10	50	70
5	100	50	-	-	50	0
6	100	100	-	-	50	0
9	100	100	-	-		
10	100	100	-	-		
12	100	100	100	-	100	50
13	100	100	40	10	60	10
21	100	70	-	-	60	40
27	100	100	100	90	20	0
29	100	100	70	-	20	0

3. Tribolium

Compound of Emb.	% killed 300	100	30 ppm	% killed with Mecarbam 300	100 ppm
1 and 2	100	88	0	72	64
3	96	76	16	72	64
4	96	84	24	72	64
6	92	80	64	72	64
9	100	100	88	68	60
13	100	80	0	48	36
15	92	84	72	48	20
17	100	52	0	64	40
27	100	100	56	48	28

Test of effectiveness as contact poison against Musca domestica (House Fly)

The agent was applied in concentrations of 300 and 100, 30 and 10 ppm by micrometer syringe (topical). The percentage of dead flies was determined 48 hours after the treatment. The results are summarized together with the results of parallel test with mecarbam in Table IX.

Table IX

Effectiveness as contact poison against Musca domestica

Compound from Embodim.	% killed				% killed with Mecarbam	
	300	100	30	10 ppm	100	30 ppm
1 and 2	100	30	-	-	25	-
3	100	100	-	-		
5	100	0	-	-		
8	100	100	-	-	20	-
9	-	100	100	95	90	55
11	-	100	100	-	95	60
12	-	100	100	-	100	40
15	-	100	100	-	45	20
23	-	100	100	-	100	75
27	-	100	100	-	95	60
29	100	100	-	-	100	40

Test of effectiveness as contact poison against Dyadercus

The agent was applied in concentrations of 100 and 30 and 10 ppm by mircometer syringe to imagines of dyadercus intermedius. The percentage of kills was determined after 3 days. Parallel tests were conducted with mecarbam. The results are summarized in Table X.

Table X

Effectiveness as contact poison against Dyadercus

Compound of Embodiment	% killed 100	30	10 ppm	% killed with Mecarbam 1000	300 ppm
	44	-	-	-	100
6	44	-		-	100
13	-	100	-	100	89
15	-	-	100	100	90
27	100	-	-	90	50

Test of effectiveness against Agriotes

The agent was applied to the dry soil in the form of a watery dispersion with a concentration of 5 ppm, and thoroughly mixed with the soil. Larvae of agriotes (wire worms) were inserted into the soil. Parallel tests were conducted with benzene-hexachloride. The percentage of fatalities was determined 4 weeks after treatment. The results are summerized in Table XI.

Table XI

Test against Agriotes

Compound of Embodiment	% killed with 5 ppm	% killed with γ-Benzene-hexachloride 5 ppm
6	100	87,5
7	100	87,5
17	100	87,5
18	100	87,5
29	100	87,5

Test of effectiveness as contact poison against Pieria brassicae (Caterpillar of the Cabbage White Butterfly)

The active agent of embodiment 6 was applied at a concentration of 230 ppm against caterpillars of the cabbage white butterfly. Parallel tests were conducted with carbaryl at a concentration of 375 ppm. Three days after the treatment the surviving caterpillars were counted.

Agent	Median # of caterpillars after 3 days
Compound of Embodiment 6 at 230 ppm	2.5
Carbaryl at 375 ppm	10.5
Untreated	66.75

Test of Effectiveness against Nematodes

The compound of embodiment 1 and 2 was tested for its effectiveness against root nodule nematodes. The host plants were tobacco and tomatoes. The agent was applied in the form of fuller earth granulate soaked in a solution of the active agent in diacetonalcohol as preparation for ears of corn. The active agent preparation was raked into the soil. If not indicated otherwise in the following table, the seedlings were planted two weeks later. The results are summarized in the following table, whereby the "root nodule index" refers to a scale, in which 0 means complete extermination of the nematodes, and 5 means no extermination.

Active Agent Concentration, kg/ha	Preparation	Root Nodule Index
28	Granulate	0.5
22.4	"	0.0
11.2	"	0.0
8.96	"	5
22.4	Corn Cob	0.8
11.2	"	0.0
8.96	"	5
4.48	"	0.0
8.96	"	0.2
4.48	"	6

* - no waiting time

At concentrations of 8.96 and 4.48 kg/ha, the compound was innocuous to tobacco plants but caused slight withering of the tips of tomato plants. However, the tomato plants exhibited good size, color and root development. The agent also caused the extermination of aphids on the plants due to the systemic effect.

Additional lab tests for insecticidal effect

The following insects were used:

Boophilus decoloratus
Lucilia sericata - blowfly, whose larvae cause myiasis in sheep
Aedes aegypti - mosquito, transmits yellow fever
Musca domestica - common house fly

Every insect was subjected to a different test:

1. Boophilus decoloratus - Larvae are kept 24 hours in close contact to a 0.1% solution of the test substance absorbed on filter paper; afterwards, the extermination was determined.

2. Two tests were conducted against Lucilia sericata, both using larvae of the first phenotype. In the first method, the larvae were exposed to a 0.1% solution - absorbed on cotton balls -, and horse serum was offered to them as food. Extermination was determined after 24 hours. In the second method, the flies are made to lay eggs on guinea pigs, and the agent is given to the guinea pigs orally. The systemic effect is determined by noting the time, after which the larvae are expelled from the skin.

3. The agent is applied to the larvae (3rd to 4th phenotype) of Aedes aegypti in water at a concentration of 10 ppm for 24 hours.

4. Female house flies (Musca domestica) are used. (The male flies are more sensitive). The flies are treated topically with 1 µl of a 0.1% solution. Extermination is determined 24 hours later.

The results of the tests are summarized in Table XII:

Table XII

Compound of Embodiment	Boophilus larvae LD_{50} %	Lucilia-larvae LD_{50} %	Aedes Imago LD_{50} %	Aedes larvae LD_{50} ppm	Musca LD_{50} %
1	0.001 0.001 0.001	0.0002 0.0002 0.0005	0.003 0.004	0.07	0.003 0.0014
15	0.0006 0.001	0.0004	0.02	<0.16	0.001 0.0008
23	0.01 0.01	0.002 0.002 0.001	0.017	0.22	<0.003
28	0.04	0.004 0.004 0.001	0.07	0.32	0.01
29	0.0006 0.001	0.0002 0.0002	0.01	0.06	0.004

Good extermination of hylemyia brassicae was achieved when cabbage plants were treated with a granulate containing 5% of the compound of embodiment 17 and 18, with 1g of granulate per plant being applied. Good extermination is also achieved when dousing the plants with 70 ml of a preparation with an active agent concentration of 500 ppm, resulting from the dilution of a 25% of emulsifiable concentrate. The compounds of embodiments 6 and 12 also resulted in good extermination of hylemyia brassicae.

Patent Claims

1. Compounds with the general chemical structure:

$$X = \underset{R}{\overset{OR^1}{P}} - Y - CH_2.CO.NR^2.CO_2R^3 \qquad (I)$$

wherein R and R^1, which may be the same or be different, are aliphatic groups with 1 to 4 carbon atoms or aromatic groups,

wherein R^2 is a hydrogen atom or an aliphatic group with 1 to 4 carbon atoms,

wherein R^3 is an aliphatic group with 1 to 10 carbon atoms, and

wherein X und Y, which may be the same or be different, are oxygen or sulphur atoms,

2. Compounds according to claim 1, wherein the groups R, R^1 or R^2 are alkoxy/-kyl, alkyl, alkenyl, halogenalkyl, or alkyl+nioalkyl groups.

3. Compounds according to claim 1 or 2, wherein R and/or R^1 is a phenyl or substituted phenyl group.

4. Compounds according to one of the previous claims, wherein R^3 is an alkyl group.

5. S-(N-Methoxycarbonyl-N-methylcarbamoylmethyl)-dimethyl-phosphonothiolothionate.

6. S-(N-Methoxycarbonyl-N-methylcarbamoylmethyl)-O-methyl-ethylphosphonothiolothionate.

7. S-(N-Ethoxycarbonyl-N-methylcarbamoylmethyl)-O-methyl-ethylphosphonothiolothionat.

8. S-(N-Ethoxycarbonyl-N-methylcarbamoylmethyl)-O-methyl-ethylphosphonothiolothionate.

9. S-(N-Ethoxycarbonyl-N-methylcarbamoylmethyl)-diethyl-phosphonothiolothionate.

10. S-(N-Ethoxycarbonyl-M-ethylcarbamoylmethyl)-diethyl-phosphonothiolothionate.

11. S-(N-Methoxycarbonyl-carbamoylmethyl)-dimethyl-phosphonothiolothionate.

12. (N-Methoxycarbonyl-N-methylcarbamoylmethyl)-dimethyl-phosphonothioate.

13. (N-Ethoxycarbonyl-N-methylcarbamoylmethyl)-O-ethyl-methylphosphonothioate.

14. (K-Ethoxycarbonyl-N-methylcarbamoylmethyl)-O-methyl-ethylphosphonothioate.

15. (N-Methoxycarbonyl-N-methylcarbamoylmethyl)-diethyl-phosphonothioate.

16. (N-Ethoxycarbonyl-N-methylcarbamoylmethyl)-diethyl-phosphonothioate.

17. S-(N-Methoxycarbonyl-N-ethylcarbamoylmethyl)-dimethyl-phosphonothiolothionate.

18. (N-Methoxycarbonyl-N-ethylcarbamoyl)-dimethyl-phosphonothioate.

19. S-(N-Ethoxycarbonyl-N-methylcarbamoylmethyl)-dimethyl-phosphonothiolothionate.

20. S-(N-Methoxycarbonyl-K-methylcarbamoylmethyl)-O-propyl-ethylphosphonothiolothionate.

21. S-(N-Ethoxycarbonyl-N-methylcarbamoylmethyl)-O-propyl-ethylphosphonothiolothionate.

22. S-(N-Methoxycarbonyl-N-methylcarbamoylmethyl)-O-butyl-ethylphosphonothiolothionate.

23. S-(N-Ethoxycarbonyl-methylcarbamoylmethyl)-O-butyl-ethylphosphonothiolothionate.

24. 3-(N-Methoxycarbonyl-N-methylcarbamoylmethyl)-O-allyl-ethylphosphonothiolothionate.

25. S-(N-Ethoxycarbonyl-N-methylcarbamoylmethyl)-O-allyl-ethylphosphonothiolothionate.

26. S-(N-Methoxycarbonyl-carbamoylmethyl)-dimethyl-phosphonothioate.

27. S-(N-Methoxycarbonyl-N-methylcarbamoylmethyl)-0-2-chloroethyl-ethylphosphonothiolothionate.

28. S-(N-Ethoxycarbonyl-N-methylcarbamoylmethyl)-0-2-chloroethyl-ethylphosphonothiolothionate.

29. (N-Methoxycarbonyl-N-methylcarbamoylmethyl)-O-ethyl-methylphosphonothioate.

30. (N-Methoxycarbonyl-N-methylcarbamoylmethyl)-O-ethyl-methylphosphonothioate.

31. S-(N-Methoxycarbonyl-carbamoylmethyl)-O-propyl-methylphosphonothiolothionate.

32. S-(N-Methoxycarbonyl-N-methylcarbamoylmethyl)-0-propyl-methylphosphonothiolothionate.

33. S-(N-Methoxycarbonyl-N-methylcarbamoylmethyl) -diethyl-phosphonothiolothionate.

34. S-(N-methoxycarbonyl-methylcarbamoylmethyl)-di-propylphosphonothiolothionate.

35. S-(N-allyloxycarbonyl-N-methylcarbamoylmethyl) -diethylphosphonothiolothionate.

36. S-(N-hexyloxycarbonyl-N-methylcarbamoylmethyl)-diethyl-phosphonothiolothionate.

37 S-(N-Ethoxycarbonyl-N-methylcarbamoylmethyl)-0-2-ethoxyethyl-ethylphosphonothiolothionate.

38. (N-Methoxycarbonyl-N-methylcarbamoylmethyl)-O-propyl-methylphosphonothioate.

39. Method for the production of a formula I compound of claim 1, wherein a N-halogenacetylcarbamate of the formula

$$Hal.CH_2.CO.NR^2CO_2R^3 \qquad \text{(III)}$$

in which R^2 and R^3 have the meaning indicated in claim 1, and Hal means chlorine, bromine or iodine, reacts either with a substituted phosphonic acid with the formula

$$\begin{array}{ccccccc} & & OR^1 & & & & \\ & & | & & & & \\ X & = & P & - & Y & - & Q \\ & & | & & & & \\ & & R & & & & \end{array} \qquad \text{(II)}$$

in which R, R^1, X and Y have the meaning indicated in claim 1, and Q is a hydrogen atom or an alkaline or ammonium or an organic cation, wherein, if Q is a hydrogen atom, an acid binder is present, or with a compound with the formula

$$\begin{array}{ccccccc} & & S & & & & \\ & & \| & & & & \\ R & - & P & - & S & & \\ & & | & & | & & \\ & & S & - & P & - & R \\ & & & & \| & & \\ & & & & S & & \end{array} \qquad \text{(IV)}$$

in the presence of an acid-binding agent and an alcohol R^1OH, wherein R and R^1 have the meaning indicated in claim 1.

40. Method according to claim 39, wherein the acid-binding agent is an alkaline carbonate or a tertiary organic base.

41. Method according to claim 39 or 40, wherein the transformation takes place in the presence of a solvent.

42. Method according to claim 41, wherein for the reaction of a formula III compound with a formula II compound water, dioxane, or an alcohol, ether, hydrocarbon, halogenated hydrocarbon, amide or nitrile is used as a solvent.

43. Method according to claim 41, wherein for the reaction of a formula III compound with a formula IV compound an excess at the R^1OH alcohol is used as solvent.

44. Pesticide, wherein such pesticide contains a formula I compound from claim 1, and a carrier substance or a thinner.

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December 5, 2006

I, Angela Christie, hereby certify that I am competent in both English and German languages.

I further certify that under penalty of perjury translation of the aforementioned document:

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from the German language into the English language is accurate and correct to the best of my knowledge and proficiency.

Angela C. Christie

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